

(11) (21) (C) 2,013,869
(22) 1990/04/04
(43) 1991/06/08
(45) 1999/07/20

(72) Tamura, Takaaki, JP
(72) Kumagai, Mikio, JP
(72) Katsuta, Akimichi, JP
(73) Institute of Research and Innovation, JP
(51) Int.Cl.⁶ B01D 53/56
(30) 1989/12/08 (319228/89) JP

(54) **PROCEDE POUR EPURER LES GAZ D'ECHAPPEMENT DES
OXYDES D'AZOTE QU'ILS CONTIENNENT**
(54) **METHOD FOR REMOVING NITROGEN OXIDES FROM
EXHAUST GASES**

(57) Disclosed herein is a method for removing nitrogen oxides from exhaust gases containing oxygen and moisture, which comprises bringing the exhaust gas into contact with hydrogenated zeolite catalysts or hydrogenated zeolite catalysts impregnated with one or more kinds of metals selected from the group consisting of copper, zinc, vanadium, chromium, manganese, iron, cobalt, nickel, rhodium, palladium, platinum, and molybdenum, in the presence of organic compounds. The zeolite should be a zeolite having a silica/alumina ratio of 5 or above. The zeolite may be any one of zeolite of Y type, zeolite of L type, zeolite of offretite-erionite mixed crystal type, zeolite of ferrierite type, zeolite of mordenite type, zeolite of clinoptilolite type, and zeolite of ZSM-5 type.

ABSTRACT OF THE DISCLOSURE

Disclosed herein is a method for removing nitrogen oxides from exhaust gases containing oxygen and moisture, which comprises bringing the exhaust gas into contact with hydrogenated zeolite catalysts or hydrogenated zeolite catalysts impregnated with one or more kinds of metals selected from the group consisting of copper, zinc, vanadium, chromium, manganese, iron, cobalt, nickel, rhodium, palladium, platinum, and molybdenum, in the presence of organic compounds. The zeolite should be a zeolite having a silica/alumina ratio of 5 or above. The zeolite may be any one of zeolite of Y type, zeolite of L type, zeolite of offretite-erionite mixed crystal type, zeolite of ferrierite type, zeolite of mordenite type, zeolite of clinoptilolite type, and zeolite of ZSM-5 type.

METHOD FOR REMOVING NITROGEN OXIDES
FROM EXHAUST GASES

BACKGROUND OF THE INVENTION

Field of the Invention

The present invention relates to a method of treating exhaust gases, especially those discharged from diesel engines, gas engines or gas turbines which contain excess oxygen and moisture as well as nitrogen oxides (abbreviated as NO_x hereinafter). The method comprises bringing the exhaust gas into contact with zeolite catalyst in the presence of organic compounds, thereby converting NO_x in the exhaust gas into harmless nitrogen gas.

Description of the Prior Art

There are several practical methods for removing NO_x from exhaust gases. For example, the selective reduction method is applied to exhaust gases from boilers which employs the $\text{V}_2\text{O}_5\text{-TiO}_2$ catalyst and ammonia gas as the reducing agent. The method applied to exhaust gases from gasoline engines consists of controlling the air-fuel ratio (hence the oxygen concentration) and removing NO_x , carbon monoxide, and hydrocarbons all at once by the use of the ternary catalyst. (See Funahiki and Yamada, "Catalysts for Automotive Exhaust Gas", Preprints of the Meeting for Theoretical Fundamental Study of Practical Catalysts,

Catalysis Society of Japan, p. 15 - 20, 1989.) The former method has an advantage of being effective for exhaust gases containing excess oxygen, but it has also a disadvantage of requiring ammonia gas as the reducing agent. Therefore, it is useful for special applications but not for general uses. Especially, it can hardly be applied to automobiles carrying a diesel engine of compression ignition type and to small- or medium-sized stationary boilers. The latter method using the ternary catalyst is not effective for exhaust gases containing excess oxygen and hence it is not of practical use for exhaust gases from diesel engines.

SUMMARY OF THE INVENTION

This invention relates to a method for removing nitrogen oxides from an exhaust gas containing oxygen and moisture, which comprises bringing the exhaust gas into contact with a hydrogenated zeolite catalyst having a silica/alumina ratio of at least 12.2 or a hydrogenated zeolite catalyst impregnated with one or more kinds of metals selected from the group consisting of zinc, vanadium, chromium, manganese, iron, cobalt, nickel, rhodium, palladium, platinum, and molybdenum, and having a silica/alumina ratio of at least 5, in the presence of an organic compound which is separately added to the exhaust gas as reducing agent, said organic compound being selected from the group consisting of hydrocarbons, alcohols, ketones, or ether, at a temperature sufficient to cause reaction between said hydrogenated zeolite catalyst and said nitrogen oxides.

DETAILED DESCRIPTION OF THE INVENTION

According to the present invention, hydrogenated zeolites are used as catalyst or catalyst support. The hydrogenation of the zeolite is carried out either by a 5 direct method or an indirect method. The former method involves the steps of washing the zeolite with mineral acids repeatedly and exchanging cations in the zeolite with hydrogen ions. The latter method involves the steps of washing the zeolite with ammonium ion- 10 containing water repeatedly, replacing cations in the zeolite with ammonium ions, and calcining the zeolite thereby volatilizing ammonia. Both the methods can be used for the present invention.

One of the most important features of the present 15 invention is to use hydrogenated zeolites. Zeolite without hydrogenation removes NO_x very little as demonstrated in Example 1 and Comparative Example 1 which follow. There are no restrictions as to the species of the zeolites to be used in the present 20 invention; it may be either synthetic one or naturally occurring one, so long as it is hydrogenated.

It is well known that the acid resistance of a zeolite depends on the silica/alumina ratio which indicates the chemical composition of the zeolite, and 25 that the smaller the silica/alumina ratio, the lower the acid resistance. It is also known that hydrogenated zeolites are hydrophobic and have the properties of

solid acids, the strength of which depend also on the silica/alumina ratio. (See Course of Catalysts, vol. 10, compiled by the Catalysis Society of Japan, published by Kodansha, 1986.) These facts may suggest 5 that the activity of catalysts supported on zeolites will greatly vary depending on the silica/alumina ratio. The present inventors found from many experiments on a variety of zeolites that desired catalysts in the present invention are obtained by hydrogenating zeolites 10 having a silica/alumina ratio higher than about 5, as demonstrated in Examples 1 and 2 that follow. In addition, more active catalysts are obtained by hydrogenating zeolites having a silica/alumina ratio higher than about 10, as demonstrated in the same 15 examples.

According to the present invention, the hydrogenated zeolite catalyst can be prepared by hydrogenating a synthetic zeolite (such as zeolite of Y type, zeolite of L type, zeolite of offretite-erionite 20 mixed crystal type, zeolite of ferrierite type, zeolite of mordenite type, and zeolite of ZSM-5 type) or a natural zeolite (such as zeolite of mordenite type and zeolite of clinoptilolite type), as shown in Examples. They are exemplary but not limitative.

25 According to the present invention, the catalyst is used in the presence of organic compounds as reducing agent. The organic compounds include hydrocarbons such

as methane, ethane, propane, butane and fuel oil as well as alcohols, ketones, and ethers. In other words, the method of the present invention permits a much wider selection of reducing agent than the conventional 5 selective reduction method which resorts to ammonia as the reducing agent.

The impregnation of metallic elements on the zeolite may be accomplished by stirring the hydrogenated zeolite (prepared as mentioned above) in an aqueous 10 solution of salts of desired metallic elements followed by separating from the solution, and drying and calcining the treated zeolite. (This method will be referred to as the first impregnation method.) Alternatively, the impregnation may be accomplished by 15 contacting the zeolite with an aqueous solution of salts of desired metallic elements and then with water containing ammonium ions and finally heating the treated zeolite for volatilizing ammonia. (This method will be referred to as the second impregnation method.) 20 The second method may be performed by reversing the order of contacting. (This method will be referred to as the third impregnation method.)

In Examples explained later, experiments were carried out using synthetic zeolites of TSM series 25 produced by Toso Co., Ltd., which include zeolites of Y type, L type, offretite-erionite mixed crystal type, ferrierite type, mordenite type, and ZSM-5 type. These

zeolites were hydrogenated by dipping in 4N hydrochloric acid at 100°C for 4 hours and then thoroughly rinsing and drying. Experiments were also carried out using natural zeolites, which include mordenite-containing 5 tuff (from Akita Prefecture) and clinoptilolite-containing tuff (from Fukushima Prefecture). The natural zeolites were hydrogenated by washing repeatedly with heated hydrochloric acid (2 mol/L) for 40 hours.

The catalytic activity of the hydrogenated zeolites, 10 with or without metallic elements supported thereon, were tested in the following manner. The powder of the hydrogenated zeolite was molded under pressure, then crashed and sieved to collect particles with diameters between 10 - 20 mesh. The sample (5 cm³) was filled in 15 a stainless steel reactor tube 10 mm in inside diameter. Through this reactor tube was passed a simulated exhaust gas composed of 0.15 vol% NO, 10 vol% oxygen, and 7.3 vol% moisture, with the balance being argon. As an organic compound as the reducing agent, propane was 20 added into this exhaust gas in an amount equivalent to 4 - 5 times the concentration of NO_x (in molar ratio). The concentrations of NO_x in gases were measured by the chemiluminescence method. The percentage of NO_x removed was calculated according to the formula below;

$$25 \quad 100(\%) = \frac{A}{B}$$

where, A = concentration of NO_x in the gas discharged
from the catalyst layer

B = concentration of NO_x in the gas entering the
catalyst layer

5 The invention will be more clearly understood with
reference to the following Examples and Comparative
Examples.

Example 1 (Removal of NO_x by hydrogenated zeolite
catalysts)

10 Experiments on the removal of NO_x by a variety of
hydrogenated zeolite catalysts were carried out. The
results are shown in Table 1. In these experiments, the
temperature of the reactor was kept at 400°C and the
flow rate of the simulated exhaust gas was 210 mL per
15 minute (equivalent to the space velocity of 2500 hr^{-1}).
It is noted from Table 1 that the percentages of NO_x
removed are zero in the cases of zeolites having
silica/alumina ratios lower than 10 and that the
percentages of NO_x removed are higher than 30% in the
20 cases of zeolites having silica/alumina ratios higher
than 12. The results indicate that the hydrogenated
zeolites themselves can remove NO_x from the exhaust gas
containing excess oxygen so long as the zeolites have
silica/alumina ratios higher than about 10 and the
25 exhaust gas is incorporated with an organic compound as
the reducing agent.

Table 1

Type of zeolite	Silica/alumina ratio	Percentage of NO_x removed (%)
Y type	5.9	0
L type	6.2	0
Offretite-erionite mixed crystal type	7.4	0
Mordenite type	10.2	1
Ferrierite type	12.2	34.0
Mordenite type	14.9	35.0
Ferrierite type	20.5	41.0
ZSM-5 type	40.0	40.0

Example 2 (Removal of NO_x by metal-impregnated
15 hydrogenated zeolite catalysts)

Experiments were carried out in the same manner as
in Example 1 using a variety of catalysts impregnated
with one or more metals selected from among nickel,
copper, manganese, chromium, cobalt, zinc, iron, and
20 vanadium. The results are shown in Table 2. It is
noted from Table 2 that hydrogenated zeolites become
more active when they are impregnated with metallic
elements. The percentage of NO_x removed is higher than
20% even when the silica/alumina ratio is lower than
25 10 (except in the case of zinc catalyst). And the
percentage of NO_x removed is higher than 60% if the
silica/alumina ratio is higher than 10 (except in the

2013869

case of zinc catalyst). Thus the percentage of NO_x removed is greatly increased when hydrogenated-zeolites are impregnated with metallic elements.

Table 2

	Metallic element supported	Kind of carrier*	Silica/alumina ratio	Percentage of NO_x removed (%)	Conversion into nitrogen gas (%)
5	Copper	A	5.9	100	100
		B	12.2	100	99
		C	14.9	100	100
		D	40.0	100	100
10	Vanadium	A	5.9	33.6	100
		B	12.2	86.8	100
		C	14.9	84.5	99
		D	40.0	86.2	99
15	Chromium	A	5.9	29.7	97
		B	12.2	46.7	99
		C	14.9	42.7	99
		D	40.0	49.3	100
20	Manganese	A	5.9	81.1	100
		B	12.2	97.9	100
		C	14.9	89.2	99
		D	40.0	99.1	100
25	Cobalt	A	5.9	20.7	98
		B	12.2	77.3	100
		C	14.9	88.4	97
		D	40.0	89.8	99
30	Nickel	A	5.9	66.2	100
		B	12.2	99.8	100
		C	14.9	87.8	100
		D	40.0	99.9	100
35	Zinc	A	5.9	13.7	97
		B	12.2	23.5	96
		C	14.9	22.3	95
		D	40.0	23.0	98
40	Iron	A	5.9	25.4	92
		B	12.2	66.5	100
		C	14.9	65.7	100
		D	40.0	68.3	97
45					

* A: Y type, B: ferrierite type, C: mordenite type,
 D: ZSM-5 type

Example 3 (Effect of space velocity on the removal of NO_x
by metal-impregnated zeolite catalysts)

Similar experiments to those in Example 2 were carried out using copper catalysts or copper-nickel 5 catalysts to examine the effect of space velocity on the removal of NO_x . No water vapor was added to the simulated exhaust gas in these experiments. The results are shown in Table 3. It is noted that catalysts on zeolites having a silica/alumina ratio lower than 10 achieve the 10 percentage of NO_x removed higher than 50% even when the space velocity is increased four-fold (up to $20,000 \text{ hr}^{-1}$). In the case of catalysts on zeolites having silica/alumina ratios higher than 10, the percentage of NO_x removed is higher than 90% at the same space velocity.

Table 3

	Metallic element supported	Zeolite (silica/alumina ratio)	Space velocity (hr ⁻¹)	Percentage of NO _x removed (%)	Conversion into nitrogen gas (%)
Copper	Type Y (5.9)		5000	100	100
			10000	96.2	100
			15000	64.5	99
			20000	51.6	98
	Ferrierite type (12.2)		5000	100	100
			10000	100	100
			15000	100	100
			20000	96.4	99
	Mordenite type (14.9)		5000	100	100
			10000	100	100
			15000	98.6	97
			20000	87.3	98
	ZSM-5 type (40.0)		5000	100	100
			10000	100	100
			15000	100	98
			20000	97.6	99
Copper-nickel	Type Y (5.9)		5000	100	96
			10000	100	100
			15000	92.5	100
			20000	63.2	98
	Ferrierite type (12.2)		5000	100	100
			10000	100	97
			15000	100	99
			20000	93.2	100
	Mordenite type (14.9)		5000	100	100
			10000	100	96
			15000	100	100
			20000	98.8	99
	ZSM-5 type (40.0)		5000	100	100
			10000	100	100
			15000	100	95
			20000	99.1	97

Example 4 (Identification of reaction products)

The exhaust gas treated by the present catalysts may contain nitrous oxide (N_2O) and nitric acid as well as nitrogen gas. To identify these compounds, the 5 treated exhaust gas was analyzed. Since the simulated exhaust gas does not contain nitrogen gas, it is possible to calculate the conversion of NO_x into nitrogen from the amount of nitrogen produced. The determination of nitrogen and nitrous oxide was carried 10 out by gas chromatography. The determination of nitric acid was carried out by alkali titration of the condensate recovered from the treated gas by cooling by ice. It was found that the amounts of nitrous oxide and nitric acid were smaller than the limit of 15 detection.

In Tables 2 and 3, the conversion of NO_x into nitrogen gas is expressed in percentage calculated under the assumption that 2 mol of NO_x removed gives rise to 1 mol of nitrogen gas. It is noted that the metal- 20 impregnated catalysts of the present invention convert NO_x into nitrogen gas almost completely.

Example 5 (Denitration by natural mordenite)

Experiments of denitration were carried out using metal-impregnated catalysts prepared from natural 25 mordenite (from Akita Prefecture) treated by the direct hydrogenation. The metal impregnation was accomplished by the above-mentioned first method. The direct

hydrogenation was accomplished by washing natural mordenite repeatedly with 2N hydrochloric acid at 100°C for 40 hours. The metals impregnated on the catalysts were prepared mostly from nitrates (except palladium chloride, rhodium chloride, chloroplatinic acid, ammonium metavanadate, and ammonium molybdate). For metal impregnation, the catalyst was dipped in the aqueous solution (1 mol/L) of a volume three times as much as that of the catalyst, at 90°C for 2 hours.

10 The conditions of experiments were as follows: The catalyst bed was prepared by filling a column, 2 cm in inside diameter and 16 cm high, with catalyst particles, 10 - 20 mesh in size. The simulated exhaust gas was passed at a flow rate of 1 liter per minute.

15 The simulated exhaust gas was composed of N₂ (80 vol%), O₂ (10 vol%), CO₂ (10 vol%), NO (0.17 vol%), and moisture produced by injecting 4 g of water per hour into the gas. The gas was preheated to the reaction temperature and incorporated with an organic compound

20 as the reducing agent.

The results are shown in Table 4. Propane used as the reducing agent is a fuel-grade commercial product composed of 92% of propane, 8% of ethane, and 0.1% of isobutane. Gas oil is a commercial product for diesel cars. Other organic compounds are commercial reagents.

Table 4

	Element supported	Reaction temperature (°C)	Name of reducing agent	Amount added (mg/min)	Ratio of Denitration (%)	Remarks
5	None	430	None	0	8	
	None	430	Propane	3.8	55	
	None	430	Gas oil	4.3	47	
	None	350	Gas oil	4.3	45	
	None	430	Gas oil	4.3	47	
	None	500	Gas oil	4.3	41	
	None	430	Ethanol	6.0	57	
	None	430	Ethylene	4.0	50	
	None	430	Acetone	5.0	47	
	None	430	n-C ₁₀ H ₂₂	7.0	55	
10	None	430	Ether	5.0	47	
	None	430	Isobutane	4.0	50	
	Copper	400	None	0	8	
	Copper	500	None	0	6	
	Copper	600	None	0	3	
	Copper	400	Propane	3.8	34	
	Copper	500	Propane	3.8	36	
	Copper	500	Propane	3.8	36	
	Copper	600	Propane	3.8	38	
	Copper	600	Propane	8.0	61	
15	Copper	600	Propane	11.4	74	
	Copper	500	Ethanol	6.0	40	
	Copper	500	n-C ₁₀ H ₂₂	7.0	50	
	Copper	500	Ether	5.0	45	
	Copper	500	Acetone	5.0	48	
	Chromium	430	None	0	15	
	Chromium	430	Propane	3.8	52	
	Nickel	430	None	0	63	
	Nickel	430	Propane	3.8	83	
	Nickel	430	Gas oil	4.3	50	
20	Nickel	430	n-C ₁₀ H ₂₂	5.0	75	
	Nickel	430	Ethanol	5.0	60	
	Iron	430	None	0	7	
	Iron	430	Propane	3.8	62	
	Cobalt	430	None	0	27	
						O ₂ = 5%

Table 4 (continued)

	Element supported	Reaction temperature (°C)	Name of reducing agent	Amount added (mg/min)	Ratio of Denitration (%)	Remarks
5	Cobalt	430	Propane	3.8	68	
	Cobalt	430	Gas oil	4.3	50	
	Cobalt	430	Ethanol	5.0	70	
10	Palladium	400	None	0	18	
	Palladium	500	None	0	18	
	Palladium	430	None	0	10	
	Palladium	430	Propane	3.8	55	
15	Palladium	430	Propane	3.8	67	
	Manganese	430	None	0	10	
	Manganese	430	Propane	3.8	75	
	Manganese	430	Propane	3.8	78	
	Manganese	430	Gas oil	4.3	50	
20	Manganese	430	n-C ₆ H ₁₄	6.0	65	
	Manganese	430	n-C ₁₀ H ₂₂	7.0	60	
	Manganese	430	Ethanol	6.0	58	
	Manganese	430	Ethylene	4.0	70	
	Manganese	430	Acetone	5.0	65	^{O₂ = 5%}
	Manganese	430	n-Butane	4.0	70	
25	Manganese	430	Isobutane	4.0	70	
	Molybdenum	430	None	0	10	
	Molybdenum	430	Propane	3.8	51	
	Molybdenum	430	Gas oil	4.3	45	
	Rhodium	430	None	0	15	
30	Rhodium	430	Propane	3.8	51	
	Rhodium	430	Gas oil	4.3	40	
	Platinum	430	None	0	10	
	Platinum	430	Propane	3.8	55	
	Platinum	430	Gas oil	4.3	46	
35	V-Mn binary	300	None	0	15	
	V-Mn binary	400	None	0	11	
	V-Mn binary	300	Propane	3.8	27	
	V-Mn binary	400	Propane	3.8	89	
	V-Mn binary	400	Propane	7.3	95	

Table 4 (continued)

	Element supported	Reaction temperature (°C)	Name of reducing agent	Amount added (mg/min)	Ratio of Denitration (%)	Remarks
5	V-Mn binary	500	Propane	3.8	85	
	V-Mn binary	400	Gas oil	4.3	60	
10	Cr-Mn binary	430	Propane	3.8	44	
	V-Ni binary	430	None	0	9	
	V-Ni binary	430	Propane	3.8	62	
15	Cr-Ni binary	430	None	0	16	
	Cr-Ni binary	430	Propane	3.8	46	
	Cr-Ni binary	430	Gas oil	4.3	33	
20	Cr-Cu binary	300	None	0	0	
	Cr-Cu binary	400	None	0	16	
	Cr-Cu binary	250	Propane	3.8	4	
	Cr-Cu binary	300	Propane	3.8	10	
	Cr-Cu binary	430	Propane	3.8	27	
25	Cr-Cu binary	300	Gas oil	4.3	27	
	Cr-Cu binary	320	Gas oil	4.3	36	
	Cr-Cu binary	430	Gas oil	4.3	27	
	Cr-V binary	300	None	0	7	
	Cr-V binary	330	None	0	8	
30	Cr-V binary	360	None	0	25	
	Cr-V binary	300	Propane	3.8	36	
	Cr-V binary	330	Propane	3.8	61	
	Cr-V binary	360	Propane	3.8	63	
	Cr-V binary	300	Gas oil	4.3	27	
35	Cr-V binary	360	Gas oil	4.3	22	
	Cr-Fe binary	300	None	0	7	
	Cr-Fe binary	330	None	0	14	
	Cr-Fe binary	360	None	0	6	
	Cr-Fe binary	380	None	0	6	
40	Cr-Fe binary	430	None	0	4	
	Cr-Fe binary	300	Propane	3.8	58	
	Cr-Fe binary	330	Propane	3.8	78	
	Cr-Fe binary	380	Propane	3.8	58	
	Cr-Fe binary	430	Propane	3.8	46	
	Cr-Fe binary	300	Gas oil	4.3	52	
	Cr-Fe binary	330	Gas oil	4.3	55	
	Cr-Fe binary	380	Gas oil	4.3	33	
	Cr-Fe binary	430	n-C ₁₀ H ₂₂	5.0	78	

Example 6 (Denitration by natural clinoptilolite)

Similar experiments as in Example 5 were carried out except that the catalysts were prepared from clinoptilolite (from Fukushima Prefecture). Results are 5 shown in Table 5.

Table 5

	Element supported	Reaction temperature (°C)	Name of reducing agent	Amount added (mg/min)	Ratio of Denitration (%)	Remarks
10	None	430	Propane	3.8	40	
	None	430	Gas oil	4.3	40	
	None	430	n-C ₁₀ H ₂₂	7.0	50	
	None	430	Ethanol	6.0	54	
	None	430	Ether	5.0	43	
	None	430	Isobutance	4.0	40	
	Iron	430	None	0	10	
	Iron	430	Propane	3.8	40	
	Iron	430	Gas oil	4.3	30	
	Chromium	430	None	0	10	
15	Chromium	430	Propane	3.8	44	
	Chromium	350	Gas oil	4.3	43	
	Chromium	430	Gas oil	4.3	50	
	Chromium	520	Gas oil	4.3	40	
	Manganese	430	None	0	8	
20	Manganese	430	Propane	3.8	67	
	Manganese	430	Ethanol	6.0	60	
	Manganese	430	Gas oil	4.3	45	
	Manganese	430	n-C ₁₀ H ₂₂	7.0	50	
	Nickel	430	None	0	51	
25	Nickel	430	Propane	3.8	70	
	Nickel	430	Gas oil	4.3	45	
	Cr-Fe binary	430	None	0	10	
	Cr-Fe binary	330	Propane	3.8	65	
	Cr-Fe binary	430	Propane	3.8	40	
30	Cr-Fe binary	330	Gas oil	4.3	47	
	Cr-Fe binary	380	Gas oil	4.3	40	

Example 7 (Denitration by catalysts hydrogenated by the indirect method)

In this example the same raw material and impregnation method as in Example 5 were used except 5 that the hydrogenation was carried out by the indirect method in the following manner. Natural mordenite rocks were crushed, and the resulting powder was dipped in an aqueous solution of ammonium chloride (2 mol/L) at 90°C for 2 hours. The powder was then heated to 600°C to 10 volatilize ammonia. The results are shown in Table 6.

Example 8 (Effect of the second impregnation method)

The catalyst was prepared from the natural mordenite as in Example 5. The zeolite was caused to support a desired metallic element and then hydrogenated 15 by the ammonium ion exchange according to the above-mentioned second impregnation method. The results are shown in Table 6.

Example 9 (Effect of the third impregnation method)

The catalyst was prepared from the same zeolite as 20 in Example 5. The zeolite was caused to support a desired metallic element according to the above-mentioned third impregnation method. The results are shown in Table 6.

Table 6

5	Example No.	Element supported	Reaction temperature (°C)	Name of reducing agent	Amount added (mg/min)	Ratio of Denitration (%)
10	7	None	430	None	0	0
	7	None	430	Propane	3.8	59
	7	None	430	Gas oil	4.3	32
	7	Manganese	430	None	0	3
	7	Manganese	430	Propane	3.8	69
	7	Manganese	430	Gas oil	4.3	55
	7	Iron	430	Propane	3.8	40
	7	Copper	430	Propane	3.8	35
15	8	Manganese	430	None	0	10
	8	Manganese	430	Propane	3.8	67
	8	Manganese	430	Gas oil	4.3	35
20	9	Manganese	430	Propane	3.8	86
	9	Nickel	430	None	0	5
	9	Nickel	430	Propane	3.8	59

Comparative Example 1 (Removal of NO_x by unhydrogenated zeolites)

Experiments were carried out under the same conditions as in Example 1 except that the zeolite was not hydrogenated. The results are shown in Table 7. It is noted that only very little NO_x was removed.

Comparative Example 2 (Removal of NO_x by hydrogenated zeolite catalysts in the absence of organic compounds)

Experiments were carried out under the same conditions as in Example 1 except that the organic compound as the reducing agent was not added. The results are shown in Table 7. It is noted that only very little NO_x was removed.

Comparative Example 3 (Removal of NO_x by metal-
impregnated hydrogenated zeolite
catalysts in the absence of
organic compounds)

5 Experiments were carried out using metal-impregnated
catalysts under the same conditions as in Example 2
except that no organic compound as the reducing agent
was added. The results are shown in Table 7. It is
noted that the percentage of NO_x removed was less than
10 10%.

Table 7

	Zeolite	Silica/ alumina ratio	Removal of NO_x (%)		
			Comparative Example 1	Comparative Example 2	Comparative Example 3
15	A	5.9	0	0	3
	B	12.2	1	7	0
20	C	14.9	0	0	4
	D	40.0	2	5	9

Designation of zeolite:

- A: Zeolite of Y type
 B: Zeolite of ferrierite type
 25 C: Zeolite of mordenite type
 D: Zeolite of ZSM-5 type

2013869

Claims:

1. A method for removing nitrogen oxides from an
5 exhaust gas containing oxygen and moisture, which
comprises bringing the exhaust gas into contact with a
hydrogenated zeolite catalyst having a silica/alumina
ratio of at least 12.2 or a hydrogenated zeolite catalyst
impregnated with one or more kinds of metals selected
10 from the group consisting of zinc, vanadium, chromium,
manganese, iron, cobalt, nickel, rhodium, palladium,
platinum, and molybdenum, and having a silica/alumina
ratio of at least 5, in the presence of an organic
compound which is separately added to the exhaust gas as
15 reducing agent, said organic compound being selected from
the group consisting of hydrocarbons, alcohols, ketones,
or ether, at a temperature sufficient to cause reaction
between said hydrogenated zeolite catalyst and said
nitrogen oxides.

20

2. A method for removing nitrogen oxides from
exhaust gas as claimed in Claim 1, wherein the zeolite
catalyst is any one of zeolite of Y type, zeolite of L
type, zeolite of offretite-erionite mixed crystal type,
25 zeolite of ferrierite type, zeolite of mordenite type,
zeolite of clinoptilolite type, and zeolite of ZSM-5
type.

**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- BLACK BORDERS**
- IMAGE CUT OFF AT TOP, BOTTOM OR SIDES**
- FADED TEXT OR DRAWING**
- BLURRED OR ILLEGIBLE TEXT OR DRAWING**
- SKEWED/SLANTED IMAGES**
- COLOR OR BLACK AND WHITE PHOTOGRAPHS**
- GRAY SCALE DOCUMENTS**
- LINES OR MARKS ON ORIGINAL DOCUMENT**
- REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY**
- OTHER:** _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.